

### **Electrode for use in electrochemical sensor**

The present invention relates to an electrode for use in an electrochemical cell. Particularly, but not exclusively, the present invention relates to an electrode which is made from a conducting composite material, the  
5 electrode being intended for use in an electrochemical sensor for the detection and measurement of free available chlorine.

With the increased demand for electrochemical sensors, the type of electrode used in electrochemical sensors has become the subject of much research, and is critical in achieving high performance in modern detection  
10 systems. The various types of electrodes currently in use differ from one another with respect to their composition, dimensions, electrochemical properties, cost, simplicity and range of analytes with which they are used. Electrochemical sensors are commonly used to detect chemical species in solution and, as a consequence, each sensor may be designed to be  
15 specific to the chemical species to be detected.

Not all electrode geometries provide a reproducible current, however, since the region immediately surrounding the electrode surface is depleted of analyte, forming what is commonly referred to as a depletion zone. Convection arising from temperature and density variations, for example,  
20 whilst reducing the depletion zone, also result in disturbance of the concentration gradient of the analyte and thus the current flowing. There are various ways of stabilising the depletion zone surrounding the electrode, including (i) forced *reproducible* convection, (ii) use of a Clark-type oxygen electrode whereby a permeable membrane is applied to the  
25 electrode, and (iii) the use of microelectrodes.

In the case of microelectrodes, due to their small size, the depletion zone around the electrode is small compared with the boundary layer due to natural convection. As a result, the rate of flux is independent of the flow

conditions. In practice, for aqueous solutions at ambient temperatures, this means that microelectrodes need to have a characteristic dimension of less than 50  $\mu\text{m}$  to fulfil this criteria. Accordingly, by making the electrode small, the need for the complex engineering usually associated with the forced  
5 reproducible convection required to stabilise the depletion zone is eliminated.

Although there are significant advantages associated with the use in electrochemical sensors of the microelectrodes described above, not least the associated rapid response times, there also exists significant  
10 disadvantages. In particular, due to their small size, low currents are generated by microelectrodes which, whilst easily manageable in a research laboratory environment, present instrumental difficulties in electromagnetically noisy measurement situations such, as operating theatres and process lines, where it is not always necessary to have a  
15 physically tiny device but where the rapid response times of microelectrodes and their relative insensitivity to convective flow are nonetheless desirable.

One solution to the above problem is the use of *arrays* of microelectrodes in parallel in electrochemical sensors. Microelectrode arrays  
20 advantageously exhibit low dependence of current on convective flow, show enhanced rates of diffusive mass transport, and have rapid response times, whilst producing an easily manageable current in realistic situations.

However, microelectrode arrays, although regularly described in research  
25 literature, are in practice expensive to manufacture, relying either on high levels of expertise in their construction, or capital intensive C-MOS manufacturing techniques (semi-conductor fabrication technology). Although the latter technique is a useful method of microelectrode array manufacture, it (i) suffers from poor design flexibility in that a new mask is  
30 required each time the design of the microelectrode array is fine tuned, and

(ii) is restricted to planar geometry and materials which are often unsuitable for application in electrochemical sensors due to hydration, ion exchange or poor biocompatibility.

5 It has, however, been noted for some time that composite electrodes made from conducting particles embedded in an insulating binder can behave in a similar way to microelectrode arrays. The use of such composite electrodes is considerably cheaper than the use of microelectrode arrays, and does not suffer from the manufacturing disadvantages of  
10 microelectrodes discussed above. In addition, the modification of both the conducting particles of the electrode and the insulating matrix by catalysts, enzymes, redox mediators or other elements conferring (i) selectivity, (ii) improved electrode reaction kinetics (iii), improved biocompatibility and (iv) resistance to fouling reagents, including but not restricted to drugs and/or  
15 biocides, is considerably easier.

Although the use of conducting composite materials as electrodes in electrochemical sensors has been the subject of much research, as far as the inventors are aware, emphasis to date has been mainly on maximising  
20 the bulk conductivity of such composite electrodes, and many experiments have been performed to increase knowledge of the relationship between the composition of the electrodes and their conductivity. In maximising the bulk conductivity of the electrodes, conventional electrochemical tools may be employed for their characterisation, and off-the-shelf electrochemical  
25 instrumentation may be used with sensors based on such materials. Furthermore, highly conductive composite electrodes minimise the Ohmic iR drop within the electrode, which in turn simplifies both data analysis and implementation in sensors. Further still, the reactance (for instance, as measured by the RC time constant) of such electrodes is minimised if the  
30 conductivity is maximised.

As well as possessing the advantages associated with low electrical resistance as detailed above, highly conductive composite electrodes are relatively easy to characterise using accepted models and, as a result, research on composite electrodes to date has emphasised the need for negligible resistance.

To date, however, there has been little consideration of the relationship between the composition of the electrodes and their electrochemical properties, such as their microelectrode array-like behaviour.

10

Microelectrode array-like behaviour can be investigated by means of voltammetric techniques, principally steady state methods, and observation of the conducting features of the composite. The fraction of the surface area that is conducting and the size of the conducting features have been quantified using the technique of conducting atomic force microscopy (C-AFM), and this has helped to show the relationship between composition of the electrode and the microelectrode array behaviour thereof.

15

In their paper "On the microelectrode behaviour of graphite-epoxy composite electrodes", *Electrochemistry Communications* 4 (2002) 245 – 250, the inventors have previously investigated the behaviour of carbon-epoxy composites, which were made in the carbon to epoxy mass ratios 40:60, 50:50 and 60:40, using C-AFM. The equivalent volume ratios are 25:75, 33:67 and 63:37, respectively. The blends covered the

20

concentration range from just above the lower percolation limit to just up to the second percolation limit. Percolation theory is mentioned herein, and is a specific type of graph theory used to model the behaviour of materials. However, it is to be noted that there are alternative, non-graph theoretical ways of describing these materials. The lower percolation limit is the value of the conducting fraction of the composite at which conduction rises sharply; that is, the point at which the insulator to conductor transition takes

25

30

place. The second percolation limit is the value of the conducting fraction at which the insulating phase is no longer continuous.

Using C-AFM, both the 50:50 and 40:60 samples have been shown to  
5 possess conducting features with a wide variety of size, shapes and spacing, but to have many features of an appropriate size and spacing to account for microelectrode array like behaviour. Since diffusion-limited current density is substantially higher for microelectrodes, this ensures that the voltammetric behaviour is dominated by these smaller features (vide  
10 infra, the rotating disc experiments).

Microelectrode behaviour of the carbon-epoxy composite electrodes has been further confirmed using voltammetry. Cyclic voltammograms typical of microelectrodes were achieved for 60:40 (dotted line) and 50:50 (solid  
15 line) carbon-epoxy composite electrodes at  $100 \text{ mVs}^{-1}$  in  $1 \text{ mol m}^{-3}$   $\text{K}_4\text{Fe}(\text{CN})_6$  with  $100 \text{ mol m}^{-3}$  aqueous KCl. To enable comparison, the currents were normalised to the mass transport limited anodic current. Qualitatively, it is apparent that the 50:50 electrode shows a sigmoidal current voltage curve on the rising part of the voltammogram, which again  
20 is consistent with microelectrode behaviour.

Although the carbon-epoxy electrode described above exhibits notable microelectrode array-like behaviour, carbon-epoxy composites show little or no response to dissolved chlorine. Where there is a response to change in  
25 free available chlorine concentration, however, sensitivity (i.e. current per unit change in concentration) is irreproducible.

There exists a need to provide an improved electrode which exhibits the advantageous effects of a microelectrode array, whilst avoiding at least the  
30 above-mentioned disadvantages associated therewith. There further exists a need to provide an electrode which provides improved detection of free

available chlorine.

Free available chlorine is defined in "Chemical Disinfecting Agents in Water and Effluents, and Chlorine Demand" No. 27 in the series "Methods for the  
5 Examination of Waste Water and Related Materials" published by the  
Department of the Environment, HMSO, 1980, ISBN 0117514934.

The present invention is based on the finding that electrodes having a  
particular composition surprisingly show improved microelectrode array-like  
10 behaviour, in particular in the detection of free available chlorine.

In accordance with a first aspect of the present invention there is provided  
an electrode comprising a metallised carbon-insulator composite.

15 In accordance with a second aspect of the present invention there is  
provided a method for the manufacture of such an electrode comprising the  
preparation of a metallised carbon-insulator composite. A composite of this  
invention can be formulated using the techniques described in the  
experimental account that follows.

20

In accordance with a third aspect of the present invention there is provided  
a free available chlorine sensor comprising an electrode made from a  
metallised carbon-insulator composite. The metallised particles of the  
composite electrode advantageously catalyse the electro-chemical  
25 reduction of free available chlorine.

The inventors have found that microelectrode behaviour becomes less  
apparent close to or above the second percolation threshold. As discussed  
in the aforementioned paper "On the Microelectrode behaviour of graphite  
30 epoxy composite electrodes", Electrochemistry Communications 4 (2002)  
245 – 250, all electrochemical sensors to date are based upon conducting

composite materials having a high conducting fraction such that they are close to or above the second percolation threshold. However, the metallised carbon-insulator composite electrodes of the present invention have compositions above but close to the lower percolation threshold.

5 Electrode compositions above but close to the lower percolation threshold of bulk conductivity are characterised by a large number of widely-spaced microscopic conducting features which leads to the microelectrode array-like behaviour.

10 The inventors have found that electrode formulation is based on the volume fraction, as opposed to the mass fraction. The volume fraction is substantially identical to the area fraction for randomly dispersed particles. The volume fraction of the metallised carbon (i.e. the conducting particles) in the metallised carbon-insulator composites of the present invention is in  
15 the range of 15 to 45%. It is preferable but not essential that the composite material has a composition such that the conducting material concentration is only just in excess of that required for bulk conductivity, i.e. just above what is called 'the percolation threshold' in percolation theory and other graph theory descriptions. This fraction may vary considerably according  
20 to the form and size of the conducting particles. It is typically of the order of 18-25% by volume of irregular carbon particles but may be below 0.1%(w/w) for high aspect ratio materials such as carbon nanotubes.

Metallised carbon-insulator composite electrodes exhibit low sensitivity to  
25 flow and are resistant to fouling. Such advantageous characteristics significantly increase the utility of sensors using this type of electrode especially where the matrix is characterised by poorly defined or time-varying convection (blood and non-Newtonian fluids generally, physiological applications, process control, food processing, and  
30 environmental monitoring). Furthermore, sensors using this type of electrode are particularly useful where the medium is poorly conducting,

and where there are surface active constituents in the matrix (physiological preparations, cell and tissue culture, and biological and environmental samples).

5 In using metallised carbon-insulator composites, the sensitivity (current per unit change in concentration) and linear range can be tuned through varying the metal or catalyst content and identity. Further, selectivity is affected by both metal or catalyst concentration and identity, and so can be altered.

10

Suitable insulating binders include: polyethylene, polypropylene, polymethylmethacrylate, silicone elastomers (e.g polydimethylsiloxane), polytetrafluoroethylene (PTFE, Teflon), polyethyleneterephthalate, polycarbonate, polyamide, polyimide, Kel-F, polycyanoacrylate, polyester, 15 mylar, Dacron and epoxy resin. The key property is that the insulator shows high electrical resistance, resists inhibition of water and has a high breakdown voltage.

It is preferred, but by no means essential, that the electrode is made from a 20 ruthenium modified carbon-insulator composite. Ruthenium modified carbon catalyst immobilised in low concentration in epoxy resin matrix has shown excellent ability to measure dissolved chlorine, hypochlorite and hypochlorous acid in swimming pool water with good selectivity in the presence of chloramines, high total organic carbon and over a wide range 25 of pH values. The device is stable despite immersion and intermittent use over several months at least. Alternatively, for example, the electrode may be made from a platinum modified carbon catalyst epoxy composite, or a rhodium modified carbon catalyst epoxy composite. It is to be understood, however, that other suitable metallised carbon insulator composites may 30 also be used. The metal component of the metallised carbon-insulator composite may comprise any of the platinum group metals.



Metallised carbon-insulator composite materials such as those disclosed above can be extruded, moulded, printed or machined into a suitable form ranging in size from sub-millimetre, i.e. around 10 $\mu$ m, to several  
5 centimetres dimensions.

The electrodes made from such composites can be used singly, or alternatively several may be used in parallel. In the case where several composite electrodes are used in parallel, elements with similar selectivities  
10 may be used or, alternatively, electrodes with differing selectivities may be used, thereby producing sensors applicable to various different analytes.

The present invention will now be described, by way of example only, with reference to the accompanying example and drawings in which: -

15

Figure 1 shows sigmoidal current voltage curves for various non-metallised composite electrodes.

Figure 2 shows current voltage curves for non-metallised composite  
20 electrodes having a more dilute formulation than those of Figure 1.

Figure 3 shows the response to stirring of a 60% (w/w) carbon epoxy composite electrode compared with a glassy carbon electrode.

25 Figure 4 is a table showing the sensitivity to flow of various non-metallised composite electrode compositions.

Figure 5 shows histograms of the conducting feature size distribution in various non-metallised composite electrodes.

30

Figure 6 shows confocal fluorescence imaging of the electrode reaction as

the potential increases.

Figure 7 shows simulated field conditions testing using a 40:60 carbon and ruthenium composite electrode. Typical calibration curve measured at pH  
5 7.1 concentrations measured against standard DPD test.

Figure 8 shows simulated field conditions testing using a 40:60 carbon and ruthenium composite electrode. Calibration curves measured at various pH concentrations measured against standard DPD test.  
10

Figure 9 is a graph showing the dependence of the diffusion limited current on the square root of the rotation rate.

### **Example**

15 Metallised carbon epoxy composites were manufactured in the following manner: -

Low viscosity epoxy resin ('Araldite' CY1300+HY1301 Ciba-Geigy, Duxford, Cambs. U.K.) was prepared according to the manufacturer's schedule and  
20 degassed under vacuum. It was then mixed with ruthenium- or platinum-modified carbon (metal content in the range 0.5 to 10% by weight) in the ratios of 22% to 45% by volume. The mixture was degassed under vacuum prior to casting. The electrodes may be inlaid discs made by casting the composite into an insulating electrode body, or conducting  
25 discs made by sectioning cast and cured composite and mounting them into an electrode, for example. For the latter, the composite was packed into plastic tubes (typically 7 mm diameter). After setting and curing according to the manufacturer's schedules, the resulting composites were sectioned with a precision diamond saw (Buehler Isomet) into 1 mm and 2  
30 mm slices. The slices were mounted on an insulating tube and electrical contact made either using silver loaded epoxy composite or a spring.

It is to be noted that the metallised carbon epoxy composites are not restricted to discs or even to an inlaid arbitrary shape since the devices still work when cast in a fairly haphazard way. The devices are only cut into a flat shape to aid analysis of their performance. The composite material can  
5 make satisfactory electrodes by printing or painting.

In Figures 1 to 6, it is shown that the microelectrode-like behaviour of the non-metallised composite electrode depends strongly on composition through the combination of voltammetry and conducting probe atomic force  
10 microscopy (C-AFM). This latter technique generates images of the surface conductivity and the conducting feature size and distribution has been measured down to sub-micrometre length scale. Significant microelectrode behaviour, notably the relative insensitivity to convective flow, compared with bulk conductors and highly concentrated dispersions is  
15 observed.

Tips for the rotated disc experiments (described below) were machined out of PVC, abraded lightly with 2500 grit emery paper, and rinsed in ethanol. Self adhesive copper tape was punched out and applied as a backing for  
20 the composite. The recesses (typically 2 mm) were filled with carbon epoxy composite and allowed to cure. The top 0.5 mm was removed with a precision diamond wafering saw. The surfaces were polished with successively finer grades of aqueous alumina slurry down to 0.05  $\mu\text{m}$ . Prior to the experiments, the electrodes were cycled in sulfuric acid (100  
25  $\text{mol m}^{-3}$ ) between the potentials of oxygen and hydrogen evolution for 10 minutes at  $1 \text{ V s}^{-1}$ , held at hydrogen evolution potential for a further 15 minutes. The electrodes were then rinsed in de-ionised water and kept wet till needed.

### 30 **Voltammetric behaviour**

Figure 1 shows sigmoidal current voltage curves characteristic of microelectrode behaviour for the 50% (w/w) non-metallised composite electrode (solid line) and the more peak shaped response shown by the 60% (w/w) formulation (pecked line). For the more dilute formulations, this phenomenon is general over the accessible timescales (dictated by the RC time constant of the electrode) whereas maximally conductive composites only show this behaviour at scan rates less than  $50 \text{ mV s}^{-1}$  (see Figure 2)

### **Response to convection**

Figure 3 compares the response to stirring of a 60% (w/w) carbon epoxy composite electrode with a glassy carbon electrode. Even this comparatively highly conductive composite shows diminished response compared with the poorly reproducible response of a bulk conductor. Stirring the electrochemical cell elicited no change in the steady state current for the lower concentration composites.

15

The convective boundary layer at a rotated disc is of uniform thickness and can be calculated from an equation due to Von Karmen in Angew. Math. Mech. 1 233 (1921). Only those conducting features which have a characteristic dimension comparable to the boundary layer thickness will contribute to the variation of current with boundary layer thickness. As the rotation speed increases, the slope of  $i_d$  vs.  $w^{1/2}$  (the Levich plot) should increase as the boundary layer thickness decreases and ever smaller features are recruited into the flow dependent regime. It is a simple matter to calculate the expected slope of these curves for different formulations based on the measured conducting area from the C-AFM data. Image analysis of the C-AFM images allows construction of a histogram of feature areas and perimeters, *vide infra*.

3 mm radius disc electrodes were used for this study. The redox probe was ruthenium (III) chloride ( $1 \text{ mol m}^{-3}$ ) in KCl ( $1000 \text{ mol m}^{-3}$ ). Using

30

published values of the diffusion coefficient ( $D = 9.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  and kinematic viscosity ( $\nu = 0.00916 \text{ cm}^2 \text{ s}^{-1}$ ) the predicted slope for a bulk conducting electrode is  $1.61 \times 10^{-5} \text{ A (rad s}^{-1}\text{)}^{-1/2}$ . Values obtained for the various composites are summarised in Figure 4.

5

As is plain from the data in Figure 4, all compositions show lower sensitivity to flow than is predicted from the known measured area fractions. This is the first direct evidence that the behaviour of these devices is dominated by microscopic conducting features. This is further confirmed by the significant non-zero intercept of the Levich plots.

10

### **Non-Faradaic responses**

It has been shown that for non-metallised composite materials of more typical composition, the capacitance of a polarised composite electrode in electrolyte solution (i.e. in the absence of electrolysable material) is related to the fractional surface area. This suggests that the dominant contribution is due to the electric double layer. For more dilute formulations, the capacitance scales with section thickness, showing that the dominant contribution is due to overlapping incomplete conducting pathways. In addition to providing an explanation for the large time constants observed with dilute conducting composites, this provides direct evidence for a qualitative difference between formulations close to the lower percolation limit, as employed by the inventor, to devices optimised for bulk conductivity.

25

### **C-AFM data**

The mean conducting fractions for formulations of carbon in epoxy are given in Figure 4. For all concentrations below 60% (w/w) there is no significant difference between the conducting area fractions found

30

experimentally and those predicted for randomly packed materials. The higher concentrations behave differently showing evidence of clumping, i.e. non-random interactions-the composite is no longer bicontinuous but contains islands of epoxy resin in a porous but continuous conducting  
5 matrix.

Histograms of the conducting feature size distribution are shown in Figure 5. The dilute formulations are dominated by features < 10  $\mu\text{m}$ .

### **Scanning Electrochemical Microscopy**

10 Both feedback mode and tip generation mode SECM micrographs show that the electrochemical reaction proceeds largely on microscopic isolated conducting features for the 40% (w/w) and the 50% (w/w) compositions. These conclusions were confirmed using confocal fluorescent microscopic examination of the electrode activity (see Figure 6), a relatively new  
15 technique discussed in Electrochemical Communications 4 886 (2002) by S.Cannan *et al.* From the latter data it is also evident that the finite, non-negligible resistance of the microelectrode-like elements is important in understanding the performance of these materials. These results underline the difficulties associated with using conventional electrochemical tools-  
20 quantitative analysis of the shape of the steady-state current voltage curves is a complex function of distributed microelectrode size and varying resistance of different microelectrode elements.

### **Metallised carbon-epoxy composite electrodes**

#### **-Detection of free available chlorine**

  
25

Ruthenium modified carbon composite electrodes show catalytic diffusion limited response to dissolved chlorine ( $\text{Cl}_2$ , HOCl and  $\text{OCl}^-$ , the exact species depending on the pH). It has been demonstrated that sensitivity is  
30 comparable to electrodes of solid platinum group metals and Pt plated

carbon. Typical calibration data is shown in Figure 7.

In sharp contrast to solid platinum electrodes, the long-term stability of both background current and slope of calibration was excellent over several  
5 months.

The electrodes were tested in a field simulation environment. Calibration curves were prepared for solutions of hypochlorite at various pH and temperatures. The electrodes were tested for response to chloramine,  
10 Total Dissolved Solids (TDS), cyanuric acid, fouling and changes in bulk convective flow.

The gradient changes little with a change in pH over a range typically found in swimming pools, as is shown in Figure 8. This is an advantage in a  
15 system where the pH is likely to fluctuate.

Total Dissolved Solids (TDS) can increase the conductivity of the water and produce a false response. A sensor that responds independently of the TDS concentration is an advantage in an environment that is frequently  
20 changing. Response to TDS in the form of KCl was investigated by addition to a solution of 2 mg l<sup>-1</sup> hypochlorous acid at pH 7.5. The response changes little with the additions and is within 10% of the initial response.

25 There was no response of the electrode to chloramine, demonstrating that only free available chlorine is measured. Water uptake of the electrode was minimal in long term tests. Field trials have shown the stability of the electrode over six months *in situ*. The electrode has shown greater stability and resistance to fouling than existing commercially available platinum  
30 sensors.

A major advantage of the low concentration formulation (i.e 40% (w/w)) is the decreased dependence of the diffusion limited current on the regime of convective flow as compared with (a) electrodes made of bulk conducting material and (b) composite electrodes where (i) the majority of conductive features are of a size that is comparable to or larger than the convective boundary layer thickness and/or (ii) the spacing between the majority of conducting features is within one order of magnitude or less than the characteristic linear dimension of the conducting feature. The low dependence of the diffusion limited current on the flow and the enhanced current density typically observed greatly increases the versatility of such devices in both analysis and in applications in batteries, fuel cells and electrosynthesis. For chemical analysis, the principal advantage is that highly engineered flow cells are not required, instruments for field analysis are therefore cheaper, more robust and provide more reliable data. Mathematical analyses of convective flow remain amongst the most intractable problems in engineering.

The results shown in Figure 9 show that these advantages are indeed apparent in the case of dilute (40% (w/w)) dispersions of ruthenium modified carbon particles (5% Ru) in epoxy resin which have demonstrable utility as sensors for freely available chlorine in aqueous solution. For similar dispersions of graphite in epoxy, the flow dependence is related to the conducting feature size, size distribution and spacing as measured by conducting atomic force microscopy. This relationship can be quantified by rotating disc electrode voltammetry. Experimental data for three different compositions of ruthenium modified carbon epoxy composites are shown in Figure 9. Hexaamine ruthenium (III) chloride ( $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ ) was used as a tracer to characterise the conducting composite electrodes since it shows thermodynamically reversible electron transfer kinetics and therefore allows geometric factors to be isolated from the chemical condition of the electrode surface, a particular problem for carbon electrodes.



### Materials and Methods

Ruthenium modified carbon (5%) was obtained from Alfa, washed in  
5 acetone (AnalAR grade) in a Soxhlet, dried at 105 °C for 12 hours.  
Voltammetric experiments were in  $\text{Ru}(\text{NH}_3)_6^{3+}$  (1 mmol dm<sup>-3</sup>, Aldrich used  
as received) in aqueous KCl (0.5 mol dm<sup>-3</sup>). The reference electrode was a  
commercial aqueous silver-silver chloride (100 mmol dm<sup>-3</sup> KCl) and a  
platinum flag served as counter electrode.

10

Electrode bodies were custom manufactured from PVC and consisted of a  
2.5 cm cylindrical mantle with 4 mm wide cylindrical recess in the centre.  
The Ru-C powder was mixed with degassed epoxy resin (Araldite CY1301,  
HY1300, originally made by Ciba-Geigy but currently under license by  
15 Robnor Resins (Swindon) in the United Kingdom) in three ratios: 40% (w/w)  
Ru-C, 50% (w/w) Ru-C, 60% (w/w) Ru-C. Each formulation was again  
degassed under vacuum and packed into the cylindrical recess in the PVC  
electrode bodies and compressed using a PTFE mandrel. After curing  
according to the manufacturer's schedule, the electrodes were sawn  
20 parallel to the surface using a low speed diamond saw (Buehler) to leave a  
packed recess 1 mm deep. Final polishing was with 2500 grit emery paper  
and successively finer alumina slurries down to 0.03 µm to obtain a mirror  
like finish. The electrode was mounted in a rotating disc electrode  
assembly (PAR) and electrical connection was established with a stainless  
25 steel spring. Final cleaning was by potential cycling between the potentials  
for oxygen and hydrogen evolution at 1 V s<sup>-1</sup> in sulfuric acid (0.5 mol dm<sup>-3</sup>)  
for 20 minutes followed by 15 minutes at the hydrogen evolution voltage.

Quasi-steady state voltammograms were recorded in the ruthenium  
30 hexaammine solution at 2 mV s<sup>-1</sup>. Diffusion limited steady state currents  
were calculated from the background corrected voltammograms.

## **Discussion**

It is clear from Figure 9 that the Levich slope for all three formulations is below that for a bulk conductor (solid line). The results for the 50% and 60% formulations are qualitatively different from the 40% (w/w) composite. Of particular significance is the lower value of the slope at speeds below 25  $\text{s}^{-1}$ . The higher concentration composites have slopes approaching the Levich line over the same rotation speeds confirming that the isolated conducting features are more densely packed and that microelectrode array-like behaviour is more evident for the 40% concentration.

These results quantitatively confirm that more dilute formulations of Ru-C particles in epoxy resin show disproportionately lower sensitivity to convective flow than the more commonly used high conducting fraction dispersions. This is due to the small size and wide spacing of many of the conducting features rendering the behaviour more like a microelectrode array.

## **Conclusion**

The totality of evidence from voltammetry, non-faradaic responses and scanning probe microscopic investigations all confirms that dilute conducting metallised carbon-insulator composites are qualitatively different in their structure and voltammetric behaviour from composites optimised for maximum conductivity. The diminished response to convection, the enhanced mass transport, ease of modification and resistance to fouling render these materials as eminently suitable for application to electrochemical chlorine sensors.

The metallised composite electrode of the present invention has numerous fields of application, most notably water treatment, food processing,

sterilisation equipment, surgical sterilisation, portable field instrumentation in water treatment and waste water treatment, waste stream remediation, industrial effluent monitoring and control, and swimming pool monitoring.

- 5 Further applications of the composite electrode of the present invention beyond electrochemical sensors include as components of fuel cells, primary and secondary cells for batteries, electrolyzers and electrochemical reactors.
- 10 The present invention is not limited to the particular features of the composite electrode described above. Elements of the composite electrode may be omitted or altered, and the scope of the invention is to be understood from the appended claims.